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DEVELOPMENT AND EVALUATION OF DIE MATERIALS FOR USE IN THE GROWTH OF SILICON RIBBONS BY THE INVERTED RIBBON GROWTH PROCESS – TASK II – LSSA PROJECT

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RCA Laboratories
Princeton, New Jersey 08540

QUARTERLY REPORT NO. 4

September 1978

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the Department of Energy.

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Prepared Under Contract No. 954901 For
JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
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PREFACE

This Quarterly Report No. 4, prepared by RCA Laboratories, Princeton, NJ 08540, describes work performed for the period 1 July 1978 through 30 September 1978, under Contract No. 954901 in the Materials and Processing Research Laboratory, H. Kressel, Director. G. W. Cullen is the Group Head and the Project Supervisor. M. T. Duffy is the Project Scientist. Others who participated in this research are S. Berkman, J. F. Corboy, H. I. Moss, R. F. Paff, M. Popov, R. A. Soltis, and H. E. Temple. The RCA Report No. is PRRL-CR-78-55.

The JPL Project Monitor is T. O'Donnell.

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SECTION I

SUMMARY

The results of emission spectroscopic analysis indicate that molten silicon (sessile drop) can remain in contact with hot-pressed Si_3N_4 (99.2% theoretical density) for prolonged periods without attaining the impurity content level of the nitride. It is interesting to note that, although MgO was used as binder (~3.8%), Mg was not found present in the silicon sessile drop in quantities much above the level initially present in the silicon source material.

The conversion of CVD silicon oxynitride to β-Si_3N_4 can be carried out at high temperature in N_2 (~1600°C), by contact with molten silicon or by a combination of these steps. Conversion in the presence of molten silicon appears preferable.

Preliminary experiments with EFG-type dies coated with CVD Si_3N_4 or CVD SiO_xN_y indicate that capillary rise does not occur readily in these dies. The same was found to be true of hot-pressed and reaction-sintered Si_3N_4 obtained commercially. However, when dies were formed by depositing CVD layers on shaped silicon slabs, a column of molten silicon (~2.5 cm high) was maintained in each CVD die while being heated (~30 min) in contact with a crucible of molten silicon. Preliminary wetting of dies appears necessary for EFG growth.

Several ribbon growth experiments were performed in our new ribbon growth facility from V-shaped dies. Both CVD Si_3N_4 and CVD SiO_xN_y coatings were used on the die parts. There is also a problem with the wetting of SiO_xN_y in the inverted ribbon growth process but not with Si_3N_4 layers. After about 90 min in contact with the melt, however, silicon flows into the defining slot in the case of SiO_xN_y coatings.

SECTION II

INTRODUCTION

The objective of this program is to develop and evaluate die materials for use in the growth of silicon ribbons by the inverted ribbon growth process (IRG) and for other applications. The major emphasis is on developing CVD coatings of Si_3N_4 and SiO_xN_y on suitable die materials and studying the stability and interaction of these layers with molten silicon. The dies are being tested in silicon ribbon growth experiments and evaluated analytically. The ribbons are being characterized electrically, crystallographically, and in solar cells. Both CVD coated dies and crucibles will be fabricated, and deposition parameters will be adjusted, where possible, to favor minimum cost.

SECTION III

PROGRESS AND TECHNICAL DISCUSSION

A. REFRACTORY SUBSTRATE MATERIALS

In our last quarterly report, we described the preparation of hot-pressed Si_3N_4 and the results of a sessile drop experiment (4 h in He at 1450°C) on this material (without a CVD coating). Since then we have obtained the results of emission spectroscopic analysis on the impurity content of the component materials both before and after this test. A listing of the impurities is given in Table 1. It is interesting to

TABLE 1. IMPURITY CONTENT (PPM) OF MATERIALS IN SILICON SESSILE DROP EXPERIMENT

Element	Si_3N_4 (Powder)	Si_3N_4 (Hot-Pressed)	Si_3N_4 (Under Silicon Sessile Drop)	Si (Sessile Drop)	Si (Source)
Al	600-6000	600-6000	600-6000	30-300	3-30
Ba	10-100	10-100	10-100		
B	30-300	100-1000	100-1000	60-600	50-500
Ca	30-300	30-300	100-1000		3-30
Cu	5-50	6-60	3-30	3-30	
Fe	10-100	15-150	20-200	10-100	0.6-6
Mg	15-150	(S)	(S)	3-30	1-10
Mn	5-50	10-100	10-100	1-10	10-100
Na	20-200				
Ni		3-30	6-60		
Sr		0.3-3	1-10		
Ti	10-100	20-200	50-500		3-30
Zr		1-10	3-30		

note that some of the impurities present in the Si_3N_4 powder source material and hot-pressed Si_3N_4 are below detection level in the silicon droplet. The aluminum content in the silicon is more than an order of magnitude lower in the silicon droplet than in the substrate. It should be noted also that, although MgO (to a level of 3.8% by weight) was used as binder in the hot-pressed substrate, the Mg content in the silicon droplet is low considering the amount of impurity available and the exposure time at the melt temperature. With the exception of Al and Fe, the impurity content of the sessile drop is not widely different from that of the silicon source. This is probably due to the relatively low reactivity of β-Si_3N_4 with molten silicon. The results of x-ray analysis in this case showed that the only phase present in the substrate was the β-phase. In general, the data indicate that molten silicon can remain in contact with hot-pressed Si_3N_4 for a considerable length of time at 1450°C without acquiring the impurity content level of the substrate. Obviously, the above levels are too high, but the results provide hope for the reduction of impurities in molten silicon when a CVD coating such as CVD Si_3N_4 or CVD SiO_xN_y is applied to the substrate surface and when the contact time with melt is substantially reduced.

Hot-pressed "silicon oxynitride" was also prepared. In this case, both the powder source material and hot-pressed composite were a mixture of phases, namely α- and β-Si_3N_4 and Si as determined by x-ray analysis. The hot-pressed material was higher in β-Si_3N_4 content than the source (powder) material. The analysis is incomplete and will be reported later. The results of sessile drop experiments on this material (without a CVD coating) show penetration of the substrate surface. Analysis of impurity content is in progress. The immediate interest in hot-pressed materials is in finding suitable substrate materials for CVD coatings. For example, CVD Si_3N_4 can be deposited on hot-pressed Si_3N_4 substrates to an appreciable thickness without cracking while CVD SiO_xN_y layers cannot. Likewise, CVD SiO_xN_y can be deposited on hot-pressed silicon oxynitride to an appreciable thickness but CVD Si_3N_4 cannot.

B. REFRACTORY CVD LAYERS

The conversion of CVD silicon oxynitride layers to β-Si_3N_4 was also studied further. Some results were also given in our last quarterly report. The results of some recent experiments are given in Table 2.

TABLE 2. RESULTS OF X-RAY ANALYSIS ON CONVERSION OF SiO_xN_y TO β-Si_3N_4

Sample	Treatment	Approximate Content α-Si_3N_4	β-Si_3N_4
CVD SiO_xN_y/graphite	1 h in N_2 at ~1600°C	25%	75%
CVD SiO_xN_y/HP-Si_3N_4	2 h in N_2 at ~1600°C	≤ 5%	≥ 95%
CVD SiO_xN_y/RS-Si_3N_4	1 h in N_2 at ~1600°C, 4 h in contact with Si at 1450°C in He	5%	95%
CVD SiO_xN_y/RS-Si_3N_4	4 h in contact with Si at 1450°C in He	20-25%	80-85%

Conversion to β-Si_3N_4 can be carried out at a high temperature in N_2 by contact with the silicon melt or by a combination of these steps. In general, conversion in the presence of molten silicon seems preferable because of a tendency for the CVD layer to become detached from the substrate when heated at 1600°C in N_2. There is also a tendency for the layer to flake or crumble, which does not happen when the conversion takes place in molten silicon.

C. CAPILLARY RISE IN CVD DIES

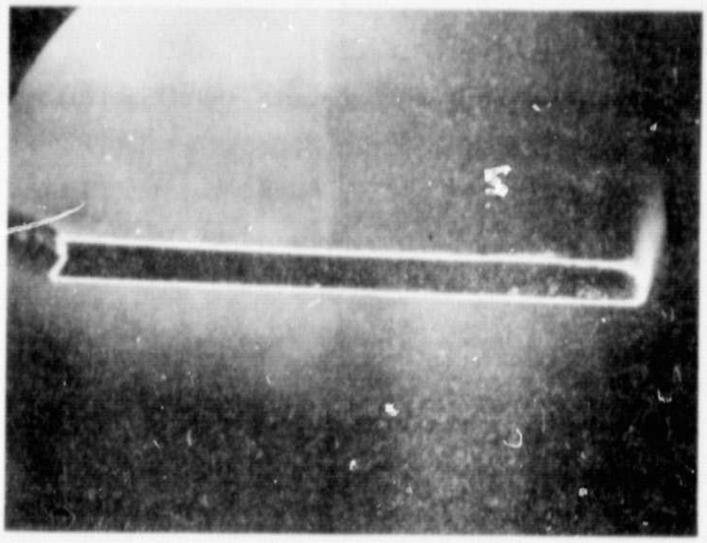
Much of our effort during this quarter was concerned with capillary rise in EFG-type dies. In preliminary experiments, capillary rise was not obtained in dies made from hot-pressed Si_3N_4, reaction-sintered Si_3N_4, silicon oxynitride, and those materials coated with CVD Si_3N_4 and CVD SiO_xN_y. These dies were maintained in contact with the silicon melt for up to three hours. Capillary rise was easily obtained in a graphite die which was used for comparison purposes. The lack of capillary action in the above dies may be due to a surface oxide, especially in the case of oxynitride. Although removal of the oxide upon exposure to molten silicon might eventually lead to capillary action, the formation of SiC on the melt from transport reactions may have resulted in retarding this action. The silicon container was a quartz crucible, and the heating element was graphite. Silicon carbide crystals were observed in the melt, and a slag was apparent on the silicon surface.

Two other approaches were attempted in order to enhance the removal rate of surface oxide and diminish the influence of silicon carbide slag. As a first approach, about 10 μm of silicon was deposited over a CVD Si_3N_4 layer on the inner walls of the die. This approach was not successful. It is not clear at this time why capillary rise was not obtained. Subsequent examination of the die seemed to indicate that the silicon layer may have drained into the melt. Consequently, the next approach was to form a die by depositing Si_3N_4 or SiO_xN_y on the surface of a shaped silicon slab (0.015" in thickness). The CVD layer was polished from both ends of the slab to form a die. This die was then positioned in the furnace as before and tested. The column of molten silicon was sustained for the duration of the experiment (~30 min). This experiment was then repeated and the same result obtained with both CVD materials. Photographs of the tops of two dies, after a light polishing step to remove SiC, are shown in Fig. 1.

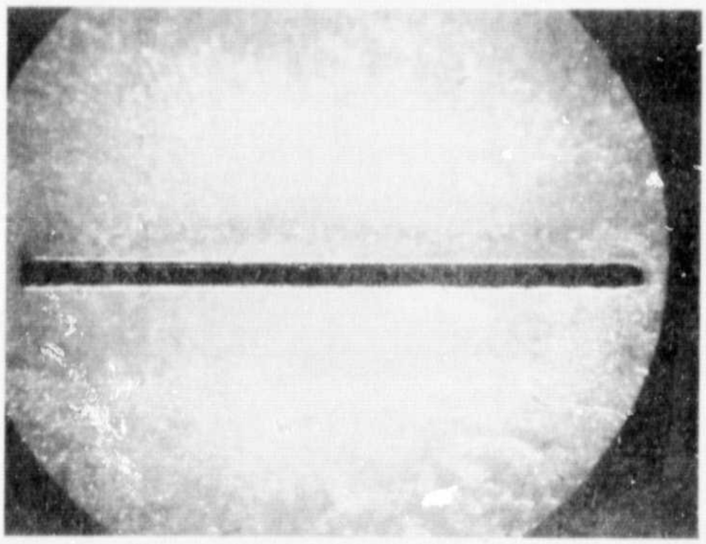
In future experiments we hope to remove silicon from the top of the CVD dies to determine if the column of molten silicon might be maintained as required for ribbon growth. Also planned is the total immersion of CVD coated dies in molten silicon prior to testing.

D. SILICON RIBBON GROWTH

The Mark II ribbon puller has been operated several times this quarter for the growth of silicon ribbon samples (by the inverted ribbon growth process) from V-shaped dies coated with CVD Si_3N_4. The initial samples grown were coated with SiC as a result of leaks in the system. However, the carbon and oxygen content in the ribbon were below the detection level of infrared analysis and lower than the levels present in the Czochralski seed material determined by the same analysis. One such specimen gave a solar cell efficiency (with AR coating) of $\eta = 11.6\%$ relative to a Czochralski wafer control which gave 13.6%. These results are similar to those reported in our second quarterly report. Several specimens have been grown after eliminating leaks. These have not been evaluated.



(a)



(b)

Figure 1. Photograph of the upper ends of two self-supporting CVD dies: (a) CVD Si_3N_4, (b) CVD SiO_xN_y.

Ribbon growth experiments with dies coated with CVD SiO_xN_y were commenced. The first problem encountered in this case was the difficulty in getting the silicon melt to wet the die and flow into the slot at the bottom of the V-shaped die. It takes approximately 90 min for sufficient wetting to occur and allow the silicon melt to spread uniformly downward into the slot. This process is accompanied by the formation of a white fiber-like growth on the thermal trimmers adjacent to the slot. This, in turn, corresponds to the conversion of SiO_xN_y to β-Si_3N_4 with the evolution of oxygen and the transport of silicon monoxide. Once wetting occurs, the ribbon growth process is not any more difficult than with Si_3N_4-coated dies.

SECTION IV

CONCLUSIONS AND FUTURE PLANS

Capillary rise in EFG-type dies coated with CVD Si_3N_4 or CVD SiO_xN_y does not readily occur unless the die parts are wet initially by contact with molten silicon. In future work molten silicon will be drawn through dies formed in this manner to determine if a column of silicon can be maintained under conditions similar to those of ribbon growth.

Silicon oxynitride layers can be converted to β-Si_3N_4 by high-temperature treatment in N_2 or by contact with molten silicon. The latter appears to be the preferred method. Conversion to the β phase prior to usage in die applications is also desirable. We plan to follow this method in preparing β-Si_3N_4 dies. Most of our future experiments will be carried out with SiO_xN_y layers.

APPENDICES

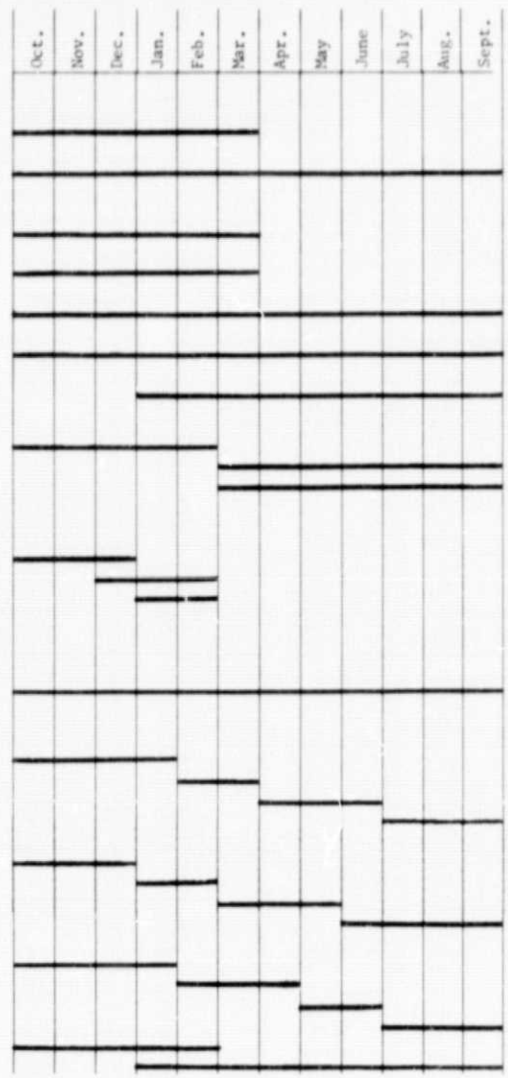
APPENDIX A

NEW TECHNOLOGY

There are no new technology items for this reporting period.

APPENDIX B

MILESTONES FOR DIE AND CONTAINER DEVELOPMENT



Key Tasks - Major Problems

1. Development and Evaluation of CVD-Si_3N_4-SiO_xN_y Systems
   - degradation and erosion rate of CVD-Si_3N_4 in contact with molten Si
   - optimization of CVD-Si_3N_4 as related to preparative conditions and post-deposition annealing
   - composition of as-deposited CVD-SiO_xN_y layers and identification of phases present after crystallization above the melting point of Si
   - degradation and erosion rate of CVD-SiO_xN_y in contact with molten Si
   - optimization with respect to preparative and annealing conditions
   - deposit above CVD layers on various die materials for the growth of silicon ribbon
   - fabricate self-supporting CVD dies and crucibles and test in contact with molten Si
2. Evaluation of Other CVD Coatings
   - identify other potentially useful coatings
   - prepare CVD coatings
   - test erosion in contact with molten Si
3. Reaction and Pressure-Sintered Materials for Use as CVD Substrates
   - Si_3N_4 with various densification aids
   - SiO_xN_y
   - Mullite
4. Characterization
   - materials characterization studies will be conducted according to that outlined in Articles 1 and 2 of Task Order No. RD-152
5. Inverted Ribbon Growth w/CVD Dies
   - Growth Rate
     - 50 cm/h
     - 100 cm/h
     - 150 cm/h
     - 200 cm/h
   - Thickness (±5 mil)
     - 40 mil
     - 30 mil
     - 20 mil
     - 15 mil
   - Ribbon Length (cm)
     - 10 cm
     - 15 cm
     - 20 cm
     - 30 cm
   - Operation of Mark I Puller
   - Operation of Mark II Puller

APPENDIX C

MANHOURS AND COSTS

Manhours and cost totals to the end of August 1978 were 4,727 and $171,070, respectively.